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Methylsiloxane Oligomers with Oxyalkyl Fragments in the Side Chain

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Summary: The dehydrocondensation reactions of α,ω–bis(trimethylsiloxy)methylhydridesiloxane with saturated primary n-alcohols in the presence of anhydrous powder-like potassium hydroxide or platinum on the carbon (Pt/C-5%) at 1:30 ratio of initial compounds, at various temperature (40–60 °C) was carried out, and methylsiloxane oligomers with n-alkyloxy substituted groups in the side chain were obtained. It was shown that completely dehydrocondensation of all active ≡Si–H groups do not take place. Dehydrocondensation reaction order, activation energy and rate constants were found. The synthesized oligomers were characterized by ^{1}H, ^{13}C NMR, Cosy and FTIR spectra data. Gel-permeation chromatography, differential scanning calorimetric, thermogravimetric and wide-angle X-ray investigations of synthesized oligomers were carried out.

Keywords: dehydrocondensation; methylhydridesiloxane

Introduction

Siliconorganic polymers having the complex valuable technical properties, in particular, high thermal and thermal-oxidative stability, low vitrification and crystallization temperatures, low dependence of various physical properties on temperature, hydrophobic nature, and stability on the action of sun light and atmosphere, are widely used in different fields of technique.

Siliconorganic polymers with siloxane structure are widely used for obtaining warm stable materials lacquer, enamel, compounds, and glue, rubbers, plastics, hermetic and composition plastics and so on.

Comb-type polymers, where on the siloxane matrix are attached branching mesogenic and non mesogenic organic groups with different length are characterized by interesting properties.[1–3]

Today there are known such organosilicon polymers, which do not contain classical mesogenic groups in the main chain, or as lateral groups, but are characterized by liquid-crystalline properties. For example dimethylsiloxane[4] and dipropylsiloxane[5,6] polymers and also cyclolinear methyl(ethyl, propyl)siloxane copolymers.[7] Thus with conducting in siloxane chain various alkyl groups, with non-mesogenic properties,[6] reception of siliconorganic polymers with liquid-crystalline properties is possible.

For synthesis of liquid-crystalline polymers trimethylsilyl terminated methylhydridesiloxane in hydrosilylation reaction frequently as an initial matrix was used.[8]

Methyl(ethyl)hydridesiloxanes are also often used in dehydrocondensation reactions for obtaining new derivatives, with organacyclosiloxane fragments, thio- and oxyalkyl groups in the side chain.[9–11]

Experimental Part

The starting materials for the synthesis of new methylorganosiloxane oligomers were α,ω–bis(trimethylsiloxy)methylhydridesiloxane and straight-chain saturated primary alcohols. The initial α,ω-bis(trimethyl-

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siloxy)ethylhydridesiloxane as a commercial product with the degree of polymerization n $\approx$ 30, primary n-alcohol (from C_6 up to C_{16}) and alkyl group terminated α-hydroxypolyethyleneglycols received from Fluka (Sigma-Aldich). The organic solvents were cleaned by drying and distillation.

FTIR spectra were obtained on a Nicolet Nexus 470 machine with MCTB detector, while the ^1H and ^{13}C NMR spectra on a "Bruker" at operating frequency of 250 MHz. All spectra were obtained with the use of $CDCl_3$ as solvent and internal standard. A Perkin –Elmer DSC-7 differential scanning calorimeter was used to determine TGA and the thermal transitions (T_g) were read at the maximum of the endothermic or exothermic peaks. Heating and cooling scanning rates were 10 °C/min.

Gel-permeation chromatographic investigations were carried out with the use of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastyragel columns (Waters, USA). Sample concentration was approximately 3% by weight in toluene and typical injection volume for the siloxane was 5 μL, standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with the known molecular weight.

Wide-angle X-ray diffractograms were carried out on a "DRON-2" instrument (Burevestnik, Saint Petersburg, Russia). A-Cu K_α radiation was measured without a filter, the angular velocity of the motor was ~2 deg/min.

Dehydrocondensation reaction of α,ω—bis(trimethylsiloxy) methylhydridesiloxane with n-alcohol

The dehydrocondensation reaction was carried out in a two-necked flask equipped with stirrer, with a catalyst inlet tube and reflux condenser connected with a gasometer. Between the gasometer and the reflux condenser a cold trap and wash bottle were installed. The initial reagents were placed in to the flask in absolute dry toluene and thermostated in an oil bath until constant temperature was achieved. Then the catalyst – anhydrous potassium hydroxide (0.1% of the total mass of the initial compounds or Pt/C – 5%) was introduced by tube. After began the elimination of hydrogen, which was collected in the gasometer and the volume was measured. The reaction was carried out at various temperatures (30÷50 °C), until liberation of hydrogen was completed. The reaction mixture was washed out several times, up to neutral medium, concentrated, then precipitated with n-hexane and subjected to vacuum up to constant weight. Because the oligomers VIII and IX were soluble in water, they have been obtained by use of catalyst platinum on the carbon, after filtration was directly precipitated from toluene solution by n-hexane.

Results and Discussions

For obtaining comb-type organosiloxane polymers containing thermotropic mezophase, the dehydrocondensation reactions of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes with saturated primary n-alcohols and alkyl group terminated hydroxypolyethyleneoxide, with various length of molecules, were studied in the presence of powder like potassium hydroxide (0.1% from total mass of initial compounds), platinum on the carbon (Pt/C-5%) and triethylamine. By preliminary heating of initial components in toluene solution at 30–80 °C temperature range in the presence of catalysts, it have been established that the side processes of polycondensation or dehydration under experimental conditions do not proceed. The dehydrocondensation reactions of α,ω-bis(trimethylsiloxy)methylhydridesiloxane with saturated alcohols were carried out at different temperatures 30, 40 and 50 °C, at the 1:30 ratios of initial components. The volume of eliminated hydrogen was measured during the reaction.

In case of use of platinum on the carbon as a catalyst in dehydrocondensation reaction of methylhydridesiloxane with n-butyl alcohol at 50 °C, was revealed that dehydrocondensation reaction proceeds less actively, in comparison with the catalyst - powder-like potassium hydroxide. Therefore, further kinetic investigations of dehydrocondensation reactions were carried out with the use of powder-like potassium hydroxide.

After the ending of dehydrocondensation reaction, the toluene solution of oligomers was washed out several times by water before neutral reaction and precipitated by n-hexane. Oligomers VIII and IX were expected as water-soluble, therefore they have been obtained in the presence of platinum on the carbon. Their toluene solutions were filtered several times and after precipitated by n-hexane.

Dehydrocondensation reactions in the presence of potassium hydroxide have been carried out at different 0.01–0.1% amounts of the catalyst. It has been established, that in case of 0.01÷0.05% potassium hydroxide, dehydrocondensation proceeds not completely and conversion of hydrogen was about ~20% and ~40% accordingly. The optimum amount of the catalyst had been chosen 0,1% from total mass of reacting compounds.

Dehydrocondensation reaction proceeds according to the following Scheme 1:

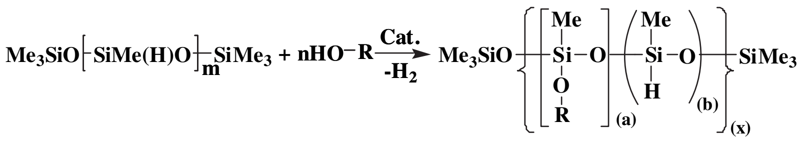
Where: R = C_4H_9 (I); C_6H_{13} (II); C_8H_{17} (III); $C_{10}H_{21}$ (IV); $C_{12}H_{25}$ (V); $C_{14}H_{29}$ (VI); $C_{16}H_{33}$ (VII); $CH_2CH_2OCH_3$ (VIII), $CH_2CH_2OCH_2CH_2OCH_3$ (IX) $-(C_2H_4O)_{20}$ $C_{16}H_{33}$ (X); $-(C_2H_4O)_{23}C_{12}H_{25}$ (XI).

The synthesized oligomers are transparent viscous liquids from R=C_4 to C_{10} or solids from C_{12}, which are well-soluble in ordinary organic solvents or in water, with $\eta_{sp} \approx 0.07 \div 0.10$. The structure and composition of oligomers, proved by elementary analysis, determination of molecular masses, FTIR, ^1H, ^{13}C and Cosy NMR spectra data. Some physical-chemical properties of synthesized oligomers are presented in Table 1. The optimum concentration of catalyst for this reaction is 0.1%. By increasing of temperature from 30° to 50 °C, the conversion of hydrogen increases from 74% up to 88% (n-hexanol) (Fig. 1). With the increase of the length of the saturated alcohol the rate and the depth of dehydrocondensation reaction decreases.

In the FTIR spectra of the synthesized oligomers, one can observe absorption bands characteristic for asymmetric stretching vibrations of ≡Si–O–Si≡ bands in the region 1020 cm^{-1}, characteristic for linear siloxane chain. In the spectra one can also observe the absorption bands for the ≡Si–H bond at 2160 cm^{-1} bond, for the $\equiv SiMe_3$ and ≡Si–Me groups at 840 and 1270 cm^{-1} accordingly.

In the spereaction of methylhydridesiloxane with n-hexanol at temperatures 30–50 °C. Where curves 1, 2 and 4 is at 50, 40 and 30 °C accordingly in the presence of 0.1% potassium hydroxide; curve 3 is at 50 °C in the presence of Pt/C (0.1%). ctra one can observe absorption bands for symmetric stretching vibrations of CH_2 groups at 2800 cm^{-1}, with the increase of the length of the side chain alkyl groups, the intensity of the signal at that region rises. For ≡Si–O–C≡ bonds one can observe characteristic bands at 1150 cm^{-1} region.

The composition and structure of synthesized oligomers were also determined by



$$Me_3SiO\left[SiMe(H)O\right]_m SiMe_3 + nHO{-}R \xrightarrow[-H_2]{Cat.} Me_3SiO\left\{\left[\begin{matrix}Me\\ |\\ Si{-}O\\ |\\ O\\ |\\ R\end{matrix}\right]_{(a)}\left(\begin{matrix}Me\\ |\\ Si{-}O\\ |\\ H\end{matrix}\right)_{(b)}\right\}_{(x)} SiMe_3$$

Scheme 1.

Dehydrocondensation reaction of α,ω-bis(trimethylsiloxy)methylhydridesiloxanes with primary saturated primary n-alcohols.

Table 1.
Elementary composition and some physical-chemical properties of oligomers.

#	(R)	**Y**ield, %	η_{sp}a)	d_2, d_1, Å	T_g, °C	T_{melt}, T_{iz} °C	$\overline{M}_{\omega}$b)(D)	Elementary composition, %,		
								C	H	Si
I	C_4H_9	96	0.04	4,18 10.10	−105	−20, +8, +28	$\underline{3907}$ 3850	$\underline{44.20}$ 44.10	$\underline{9.12}$ 8.98	$\underline{22.47}$ 22.21
II	C_6H_{13}	95	0.04	–	−120	−52	$\underline{4564}$ 4500	$\underline{50.46}$ 50.21	$\underline{9.92}$ 9.65	$\underline{19.66}$ 19.32
III	C_8H_{17}	94	0.05	–	–	–	$\underline{4988}$ 5000	$\underline{54.82}$ 54.43	$\underline{9.57}$ 9.23	$\underline{17.99}$ 17.65
IV	$C_{10}H_{21}$	96	0.07	–	−42	+0.5	$\underline{5553}$ 5400	$\underline{57.46}$ 57.20	$\underline{10.84}$ 10.73	$\underline{16.16}$ 15.91
V	$C_{12}H_{25}$	94	0.07	3.63–4.00t 6.80; 8.50;11.23 16.53;32.2	−17	0 +18	$\underline{6014}$ 5800	$\underline{59.84}$ 59.41	$\underline{11.15}$ 10.86	$\underline{14.93}$ 14.59
VI	$C_{14}H_{29}$	95	0.08	–	–	–	$\underline{6630}$ 6500	$\underline{62.24}$ 61.93	$\underline{11.45}$ 11.11	$\underline{13.54}$ 13.30
VII	$C_{16}H_{33}$	95	0.08	3.83–4.09t 7.53;12.80 28.3;35.0	+24	+30 +48	$\underline{7247}$ 5459	$\underline{64.23}$ 64.05	$\underline{11.70}$ 11.63	$\underline{12.39}$ 11.75
VIII	$OC_2\ H_4OCH_3$	92	0.07	–	–	–	–	$\underline{35.20}$ 34.86	$\underline{7.57}$ 7.23	$\underline{23.06}$ 22.67
IX*	$(OC_2\ H_4)_2\ OCH_3$	93	0.08	–	–	–	5460 (1,65)	$\underline{50.98}$ 50.05	$\underline{6.27}$ 5.56	$\underline{14.86}$ 14.47
X*	$(OC_2\ H_4)_{20}\ OR'$	94	0.10	–	+45	–	21530 (5,65)	$\underline{57.05}$ 56.68	$\underline{9.78}$ 9.43	$\underline{3.52}$ 3.17
XI	$(OC_2\ H_4)_{23}OR''$	94	0.10	–	+18	+25 +42	–	$\underline{55.28}$ 55.12	$\underline{9.60}$ 9.17	$\underline{3.17}$ 3.09

* In 1%-solution of toluene at 25 °C (VIII and IX in water ($m = 20$, $R' = C_{16}H_{33}$; $n = 23$, $R'' = C_{12}H_{25}$,).
in numerator, there are calculated values in denominator experimental values.
*Average molecular masses were obtained by GPC method.

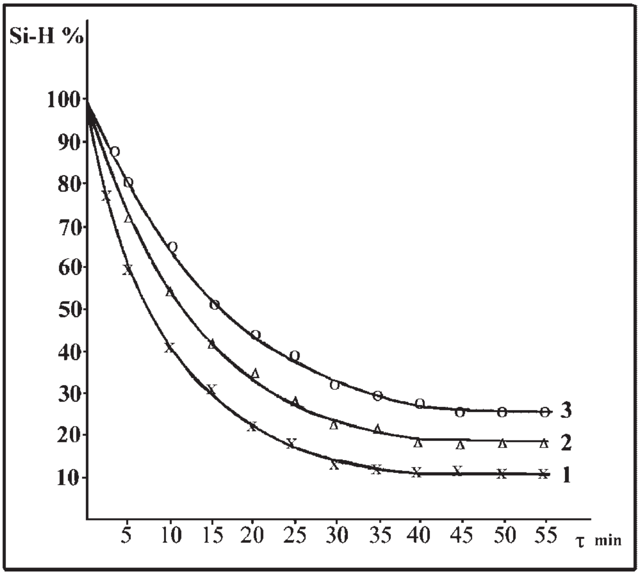
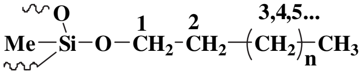


Figure 1.
Dependence of hydrogen conversion on the time, during dehydrocondensation.

^{1}H, ^{13}C and Cosy NMR spectral data. Consider the fragment:



$$\mathrm{Me{-}\overset{O}{Si}{-}O{-}\overset{1}{CH_2}{-}\overset{2}{CH_2}{-}\overset{3,4,5...}{(CH_2)_n}{-}CH_3}$$

in the ^{1}H NMR spectra of oligomers I–VII, passing from C_4 to C_{16}, appearing of additional new signals do not observe. In the ^{1}H NMR spectrum of oligomer I, one can observe singlet signal with chemical shift $\delta = 0.12$ ppm, which is characteristic for $\equiv$Si–CH_3 protons; triplet signal with chemical shift $\delta = 0.85$ ppm, which is characteristic for methyl protons of alkyl group; singlet signal of protons bounded with C_3 carbon atom with the centre of chemical shift $\delta = 1.25$ ppm; signal with chemical shift $\delta = 1.55$ ppm, characteristic of C^2H_2 methylene-group proton; singlet signal with chemical shift $\delta = 3.7$ ppm characteristic for protons in methylene-groups in OC^1H_2 fragment.

In the ^{1}H NMR spectra of oligomer II–V one can observe the overlap of signals for methylene protons at $\delta = 1.25$ ppm in C^3H_2 and C^1H_2 fragments. Analogous overlap occurs in a case of oligomer VII (n-oxyhexadecanol), where overlap the signals from C^3H_2 up to including $C^{15}H_2$.

In the ^{13}C NMR spectra of oligomer I (Fig. 2), one can observe signals for carbon atom in Si–Me fragment with chemical shift $\delta = 2.6$ ppm; for carbon atom in CH_3 fragment, with chemical shift $\delta = 12.42$ ppm; in C^3H_2 fragment - $\delta = 17.34$ ppm, fragment C^1H_2 - $\delta = 32.96$ ppm; OC^1H_2 fragment - $\delta = 60.8$ ppm.

In the ^{13}C spectra of oligomer II–V one can observe the signal of carbon of methyl-group bounded with silicon, with chemical shift $\delta \approx 4.55$ ppm; the signals of C^3H_2, C^5H_2, with chemical shift $\delta =$ 12.42 and $\delta =$ 21.08 ppm; for C^4H_2 - $\delta =$ 23.91; C^3H_2 - $\delta = 30.1$ ppm; C^2H_2 - $\delta = 30.8$ ppm and for OC^1H_2 - $\delta = 60.95$ ppm. The ^{13}C NMR spectra of oligomer VII looks easier, because one can observe the overlap of signals of carbon atoms from C^4H_2 up to $C^{12}H_2$, with chemical shift $\delta \approx 29.8$ ppm; signal of carbon atom in $\equiv$Si–Me fragment with chemical shift $\delta = -4.90$ ppm; signals with chemical shifts: $\delta = 63.11$; 33.2; 30.1; 23.07 and 14.47 ppm correspond to carbon atoms in C^1H_2, C^2H_2, C^3H_2, C^4H_2, C^5H_2 and $C^{16}H_2$ fragments accordingly.

In the ^{1}H NMR spectra of oligomer VIII-IX additionally one cane observe signal characteristic for $O\underline{CH_3}$ groups with the center of chemical shift $\delta = 3.2$ ppm, multiplet signal for $\underline{CH_2}O$ groups with center of chemical shift $\delta = 3.5$ ppm. For oligomer X and XI one can observe additionally multiplet signal with center

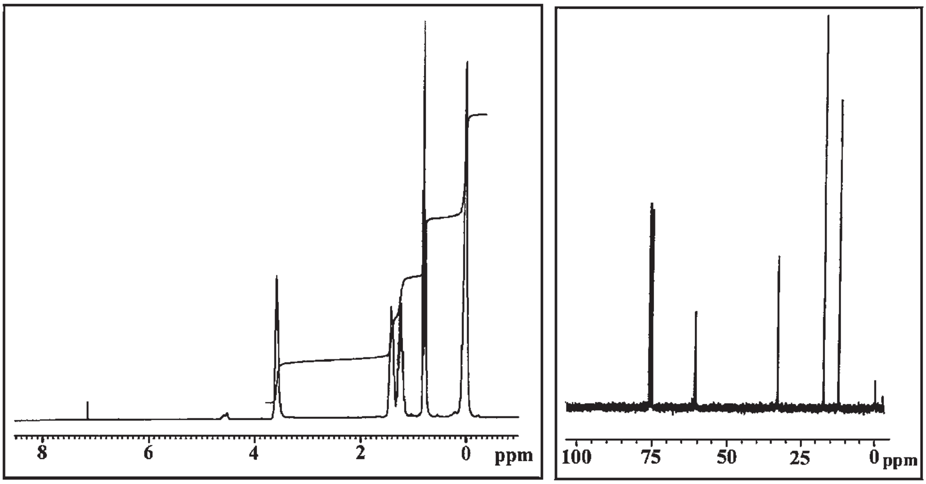


Figure 2.
^{1}H and ^{13}C NMR spectrum of oligomer I.

of chemical shift $\delta = 1.25$ ppm and analogous overlap occurs in a case of methylene protons in alkyl fragment, singlet signal of methyl protons in alkyl side fragment with chemical shift $\delta = 0{,}8$ ppm and multiplet signals with center of chemical shift $\delta = 3{,}5$ ppm characteristic of oxymethylene groups (Fig. 3).

In the ^{13}C NMR spectra of oligomer IX in the fragment $\equiv\mathbf{Si{-}O{-}CH_2^1{-}CH_2^2{-}OCH_2^3{-}CH_2^4{-}O{-}CH_3^5}$ one can observe resonance signal with chemical shift $\delta \approx 4.3$ ppm for carbon of methyl group at silicon atom and signals at $\delta \approx 57.4$ ppm ($\underline{C}H_3^5$), $\delta \approx 60.2$ ppm ($\underline{C}H_2^1$), 70.9 ppm ($\underline{C}H_2^2$) (Fig. 3).

In ^{1}H NMR spectra of oligomer VIII and IX one can observe the overlap of methylene protons at $\delta \approx 1.15$ ppm in alkyl side chain; multiplet signals with the center of chemical shift at 3.85; 3.7 and 3.5 ppm characteristic for methylene protons in $\equiv Si{-}O{-}\underline{CH_2}{-}$, $O{-}CH_2{-}\underline{CH_2}{-}$ and $O{-}\ \underline{CH_2}{-}$Alkyl units.

It was established, that at initial stages the dehydrocondensation reaction is of the second order. Dehydrocondensation reaction rate constants and temperature coefficient were determined: $k^0_{30C} \approx 0.4663$; $k^0_{40C} \approx 0.7002$; $k^0_{50C} \approx 1.00$ mol/l·s; $\gamma \approx 1.5$ ($R = n\text{-}C_6H_{13}$).

From the dependence of the logarithm of rate constants on the reverse temperature, activation energy of the dehydrocondensation reaction was calculated and it is equal to $E_a \approx 31.60$ kJ/mol. This value of activation energy is near with the value of activation energy of the dehydrocondensation reaction of methylhydridesiloxane with allyl alcohol, which is equal to $E_{act} \approx 29.2$ kJ/mole.[11]

For some synthesized oligomers GPC investigation were carried out and it was shown that oligomers have mono- and bimodal molecular weight distributions, which are changing in wide range: $D = 1{,}654 \div 5{,}65$; $\overline{M}_n = 1{,}077 \div 4{,}564 \times 10^3$, $\overline{M}_\omega = 5{,}459 \div 21{,}53 \times 10^3$, $\overline{M}_z = 4{,}564 \div 16{,}62 \times 10^3$ and $\overline{M}_y = 5{,}093 \div 17{,}11 \times 10^3$.

For some synthesized oligomers differential scanning calorimetric investigations were carried out. From calorimetric curve of oligomer I one can observe that the first temperature transition occurs at $T_g \approx -105\,^\circ C$ and it corresponds to glass transition temperature; there are three temperature transitions with endothermic peaks at $-20\,^\circ C$ which may be corresponds to melting temperature, endothermic peaks at $+8\,^\circ C$ and $+28\,^\circ C$ may be corresponded to isotropization temperatures and it indicates on pseudo-mesomorphic nature of oligomer I (see Table 1).

For oligomer II with oxyalkyl side groups one can observe the first maximum of temperature transition at $-120\,^\circ C$, which corresponds to glass transition temperature; there is also mesomorphic transition

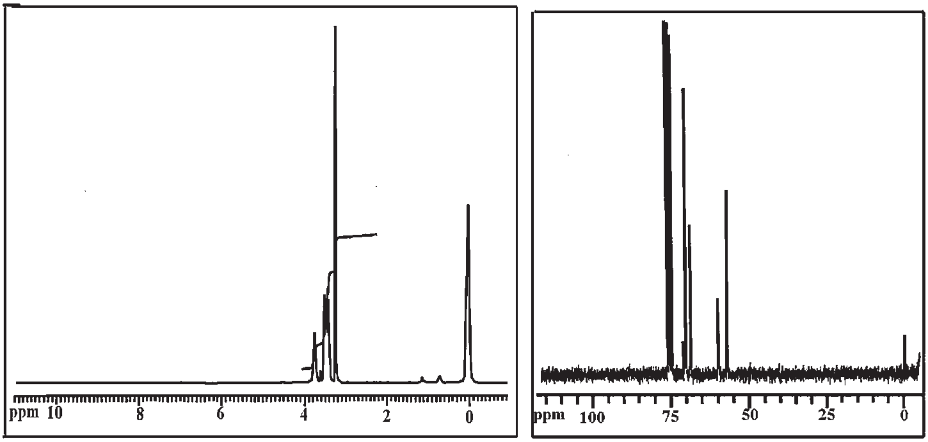


Figure 3.
^{1}H and ^{13}C NMR spectrum of oligomer IX.

with endothermic peak at +50 °C. With an increase of the length of side substituted groups the glass transition temperature rises.

Wide angle X-ray investigations for synthesized oligomers have been carried out and it was shown that for oligomer I one can observe two diffraction halos with maximums $d_1 = 10.10$ Å and $d_1 = 4.18$ Å, characteristic for amorphous systems. As for oligomers V and VII one can observe clear reflexes characteristic of crystalline systems and widened amorphous halo of amorphous part of oligomers.

In general, there are two factors which determine the formation of crystalline phase. The first is the tendency of structure to packing and the second one is intermolecular interaction. In our case the formation of crystalline phase may be promoted by the packing of side substituted groups, but it must not be ignored the intermolecular interaction of substituted side groups. In more cases intermolecular interactions are more important for crystallization. The packing in synthesized oligomers will be facilitated, because the synthesized oligomers have partially regulated structure of substituted groups, compactness and linear structure of side groups. Roentgenographic data is in conformity with differential calorimetric data and shows that at definite values of the length of side substituted groups the oligomers reveal pseudo-crystalline nature.

Thermal stability of oligoalkoxysiloxanes is determined by the presence of $\equiv$Si–O–C$\equiv$ bonds and by the nature of groups at silicon atoms. Stability of –O–$C_{alk}\equiv$ bond slightly is reduced by the increasing of electro donor nature of alkyl groups. Therefore, during the heating of methylalkoxysiloxanes the destruction of this bond must be proceeded.[12] For synthesized oligomers the thermogravimetric investigations have been carried out and it was shown that 5% mass-losses of oligomers one can observe in the temperature range 250–280 °. The main destruction processes of oligomers proceeds in the range 320–500 °C. With an increase of the length of side substituted group's final mass-losses of oligomers rises and the thermal-oxidative stability of oligomers decreases.

Conclusions

Thus, by catalytic dehydrocondensation of α,ω-bis(trimethylsiloxy)methylhydridesiloxane with various length of primary saturated alcohols methylsiloxane oligomers with oxyalkyl groups in side chains were obtained; it was established that at definite values of the length of side substituted groups the oligomers revealed pseudo-crystalline nature.

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